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Synthetic Organic Chemicals

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Hexasubstituted Ethanes

HEXASUBSTITUTED ethanes have received a great deal of attention since Gomberg, in 1900, first prepared hexaphenylethane and discovered that it dissociates into radicals containing trivalent carbon. Though colorless in the solid form, it dissolves in most organic solvents with a distinct yellow-orange color. It is apparently unsaturated, for it combines very readily with free oxygen to form a peroxide $(C_6H_5)_3CO \cdot OC(C_6H_5)_3$; with halogens to form triphenylmethyl halide; with hydrogen, in the presence of finely divided platinum, to form triphenylmethane; with nitric oxide to form a nitroso compound; and with many other reagents to form compounds of similar types. It forms addition compounds with organic solvents, paraffins, olefins, ethers, aldehydes, ketones, esters, nitriles, and other radicals.

All of these properties point to the fact that hexaphenylethane, in solution at least, exists as triphenylmethyl. Careful analysis and observation have shown that it exists as triphenylmethyl to the extent of 5 to 17 per cent near room temperature. Taking everything into consideration, it appears that these addition compounds are "molecular combinations," wherein the second component is retained through the "residual affinity" in the triphenylmethyl molecule.

Later study has produced a long list

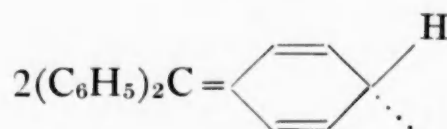
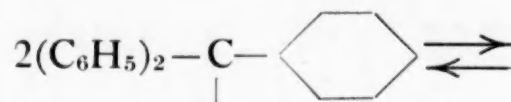
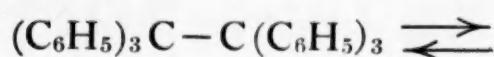
of triarylmethyls and related compounds, which show the same general properties as triphenylmethyl, and many of which show them to a greater degree. Thus diphenylbiphenylmethyl, phenyldibiphenylmethyl, and tribiphenylmethyl exist in the monomolecular state to the extent of 15, 80, and 100 per cent, respectively. Many other triarylmethyls also are monomolecular to a large degree. Derivatives of anthraquinone, xanthone, thioxanthone, and acridine have been investigated and found to contain trivalent carbon atoms. However, some of these compounds have properties different from the rest of the series, which differences are sometimes difficult to explain. Thus, while triphenylmethyl forms such a variety of addition compounds, other triarylmethyls, which are monomolecular to a much greater degree than is triphenylmethyl, fail to form such compounds. However, it seems likely that a high degree of dissociation of the hexaarylethane is indicative of the fact that in the resulting triarylmethyl, the affinity of the trivalent carbon atom is all utilized within the radical itself; consequently, there remains very little, if any, residual affinity for outside combinations, whether it be radical to radical or radical to something else.

A consideration of the factors influencing the degree of dissociation of hexaarylethanes shows that they are not so

simple as was originally supposed. The principal factor is the nature of the aryl or other substituting groups. For instance, introduction of methoxy groups in the rings shows the enhancing influence of oxygen in the aryl groups on dissociation, yet two methoxy groups in the same ring have no more influence than has one. As was previously mentioned, substitution of the phenyl groups by biphenyl groups increases the degree of dissociation. These and other data indicate that dissociation is favored by the weight and complexity of the substituting groups. However, while triphenylmethyl is monomolecular to the extent of 5 to 17 per cent, phenylxanthyl is monomolecular to the extent of 75 per cent; yet a closely related compound, phenylbiphenylenemethyl, is completely dimolecular.

The factors which influence the equilibrium between the monomolecular and the dimolecular phase of the same radical are the nature of the solvent, the concentration of the solute, and the temperature of the solution. In some instances the influence of the solvent is appreciable. The dissociating influence of nitrobenzene and benzene is much greater than that of cyclohexane. As regards concentration and temperature, their influence is in accord with what one would expect: the higher the concentration, the less is the dissociation; and the higher the temperature, the greater is the dissociation. The influence of these two factors is quite appreciable and fairly uniform.

The fact that hexaarylethanes, colorless in the solid state, give colored solutions in organic solvents has been explained by various theories. The most satisfactory explanation is that following dissociation, there is rearrangement of the benzenoid triarylmethyl into the quinoid form, which is colored. Thus, the cause of color is the formation of the quinoid structure in the triarylmethyl.



The preparation of hexasubstituted ethanes involves many interesting and often difficult syntheses. The classical method consists of forming a triarylcarbinol from an aryl Grignard and a diaryl ketone, then reacting the carbinol with PCl_3 , PBr_3 , HCl , or acetyl chloride to form the corresponding chloro- or bromomethane. The ethane is then formed by removing halogen with molecular silver, iron, magnesium, zinc, mercury, or copper. Silver is the most generally used and successful of these reagents.

In recent years, much interest has been shown in ethanes with aliphatic substituents, but in many cases the classical method of synthesis has failed to produce the desired ethanes. This is due to the fact that such ethanes are very susceptible to rearrangement and the rearrangement products are often obtained instead of the ethanes. A more recent method that has worked in some cases depends upon the reduction of the requisite carbinols with vanadous, chromous, or titanous salts. In the case of the most unstable ethanes, even this method also leads to the formation of the rearrangement products.

The most satisfactory method of synthesis of ethanes substituted with aliphatic groups, especially those containing acetylenic groups, is to react a trisubstituted bromomethane or chloromethane with sodium amalgam or sodium-potassium alloy to form the metal alkyl. The latter compound reacts with tetramethylethylene bromide to give the desired ethane. This method is

general for acetylenic ethanes where the necessary halogen intermediate can be obtained. In cases where the halogen compounds are too unstable to prepare, the methyl ethers of the intermediate carbinols usually can be prepared in good yields from the carbinols, methyl alcohol, and sulfuric acid. These ethers are readily split with sodium amalgam

to give the desired metal alkyl, which can then be coupled with tetramethylethylene bromide.

The alkyl-substituted ethanes show the same general properties as the aryl-substituted ethanes. Increase of molecular weight of the groups, branching of the chains, and unsaturation generally increase the tendency to dissociate.

Eastman Organic Chemicals as Analytical Reagents

XXXVII REAGENTS FOR HALOGENS

TRIPHENYLTIN CHLORIDE

Allen and Furman, *J.A.C.S.*, **54**, 4625 (1932)

When an alcoholic solution of triphenyltin chloride is added to a fluoride solution, triphenyltin fluoride is precipitated.

An aqueous solution of the fluoride is diluted with 95% ethyl alcohol until the alcohol comprises 60-70% of the volume. To this solution, heated to boiling, is added about twice the calculated amount of triphenyltin chloride (1% solution in 95% ethyl alcohol), which is also heated to boiling. The beaker is covered and allowed to stand overnight, as the reaction is slow. The solubility of the fluoride is lowered by packing the beaker in ice. The precipitate, after filtering and washing with 95% ethyl alcohol saturated with triphenyltin fluoride, is dried and weighed. The conversion factor of precipitate to fluorine is 0.05153.

SODIUM ALIZARINSULFONATE

Barr and Thorogood, *ANALYST*, **59**, 378 (1934)

Fluorine in water may be detected and the quantity estimated by means of sodium alizarinsulfonate and zirconium oxychloride. The reagent is prepared by mixing 1 cc. of a 1% aqueous

solution of sodium alizarinsulfonate and 3 cc. of a zirconium solution (3.53 grams $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 100 cc. of water) and diluting to 200 cc. To 50 cc. of the unknown solution are added 2.5 cc. of concentrated hydrochloric acid and sufficient of the reagent to produce a permanent pink color. The color is matched against that given by standards run concurrently.

RESORUFIN

H. Eichler, *ZEIT. ANAL. CHEM.*, **99**, 272 (1934)

Resorufin exhibits an intense yellow-red fluorescence in alkaline solution which is destroyed by either chlorine or bromine due to the formation of blue tetrahalogenated resorufin.

For the detection of chlorine or bromine in air or gas, the gas is drawn through an alkaline solution of resorufin. If either of the halogens is present, the fluorescence disappears and the blue color is immediately formed. For quantitative results, the volume of air necessary to complete the reaction with a definite quantity of test solution is measured and the halogen content determined.

This method is also suitable for use with colored solutions, since the disappearance of the characteristic fluorescence is readily observed.

Immersion Media for Determining Refractive Index

THE immersion method for determining the refractive index of a crystalline material has proved very popular for general laboratory work. It is simple and of sufficient accuracy to be of great aid in identification of unknowns.

In using this method, it is important to be certain of the exact value of the liquids used for reference. For the convenience of investigators, we have selected from the Eastman Organic Chemical List No. 26 a number of liquids recommended for this purpose and tested accurately the refractive index of them as supplied. The accompanying list, which presents these results, is available for distribution in mimeographed form.

Since most of the compounds chosen are relatively stable, there is little likelihood of change in the refractive index, necessitating checking with a refractometer only occasionally.

For the higher refractive indices, various mixtures are ordinarily employed.

Any desired index may be obtained by using the correct proportions of the different compounds, but as such mixtures are more subject to change and require regular checking, they are not included. The work of checking organic compounds is being continued in order to amplify, if possible, this list.

LIQUIDS FOR REFRACTIVE INDEX DETERMINATIONS

<i>Liquid</i>	<i>N_D at 23° C.</i>
467 Methyl Alcohol	1.3279
Water	1.3328
297 Acetone	1.3598
1135 Hexane	1.3750
2215 Heptane	1.3868
132 Ethylene Chloride	1.4417
P337 Chloroform	1.4430
684 Trimethylene Chloride	1.4470
1191 Cineol	1.4552
339 Glycerol	1.4671
P1905 Decahydronaphthalene	1.4750
T2009 Iso-Amyl Phthalate	1.4870
241 Tetrachloroethane	1.4912
T460 Xylene	1.4957
777 Benzene	1.4982
T519 Pentachloroethane	1.5006
465 Anisole	1.5150
70 Chlorobenzene	1.5218
261 Trimethylene Bromide	1.5220
130 Ethylene Bromide	1.5353
193 o-Nitrotoluene	1.5440
387 Nitrobenzene	1.5506
T461 Xylidine	1.5559
1517 Tri-o-cresyl Phosphate	1.5560
43 Bromobenzene	1.5578
253 o-Toluidine	1.5700
25 Aniline	1.5840
45 Bromoform	1.5940
216 Quinaldine	1.6088
152 Iodobenzene	1.6168
77 Cinnamaldehyde	1.6190
218 Quinoline	1.6239
72 α -Chloronaphthalene	1.6318
46 α -Bromonaphthalene	1.6569
167 Methylene Iodide	1.74